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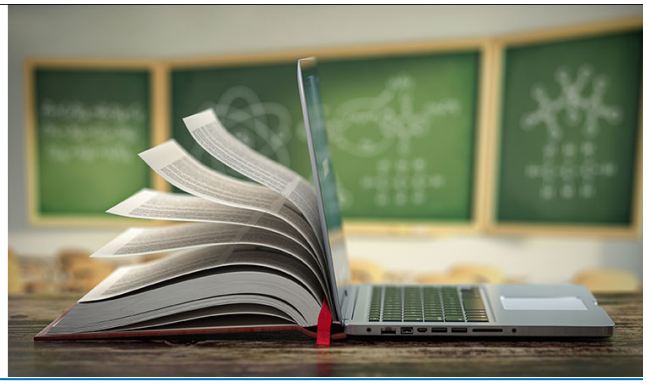
To cite this article: D V Pyrin *et al* 2021 *IOP Conf. Ser.: Mater. Sci. Eng.* **1029** 012055



Identification of the second phases formed in VDM® alloy C-4

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Abstract. The electrochemical extraction of the second phase in the VDM® alloy C-4 alloy has been studied by transmission and scanning microscopy, as well as by X-ray phase analysis. It was found that annealing, which consists in heating up to 850 ℃ with further holding for 32 hours and cooling in a furnace, leads to the precipitation of a second phase in VDM® alloy C-4 alloy. It can lead to embrittlement and a general decrease in the corrosion resistance of the alloy. The precipitation of the anode deposit (the second phase in the samples of the VDM® alloy C-4 alloy after annealing) and its identification was carried out by the methods indicated above.

1. Introduction

VDM® alloy C-4 belongs to the group of nickel-based alloys with high corrosion resistance. VDM® alloy C-4 is a nickel-chromium-molybdenum alloy with outstanding high temperature stability, as evidenced by its high ductility and corrosion resistance even after aging in the range of 649 to 1038 ℃.

In alloys of the Ni-Cr-Mo system, in addition to the solid solution based on nickel, carbide ($Me_{12}C$, $Me_{23}C6$) and intermetallic phases (σ-phase, μ-phase and P-phase, as well as the ordered $Ni_2(Cr, Mo)$ phase) can be formed. The precipitation of a solid solution with a body-centered cubic lattice based on chromium is found less frequently [1, 2]. However, most of the studies about the phase composition of the VDM® alloy C-4 are devoted to the $Ni_2(Cr, Mo)$ phase, which can be formed in the range of 350 - 650 ℃ [3 - 5]. There are conflicting data about the phases that precipitate at higher temperatures. This is largely due to the Ni-Cr-Mo phase diagram. According to it, VDM® alloy C-4 remains in a single-phase state in a wide range of temperatures, and even at temperatures of 600 - 900 ℃, the precipitation of second phases is not expected in it [6, 7]. The presence of $Me_{12}C$ carbide in VDM® alloy C-4 was recorded experimentally in [4]. In the work [8], a comprehensive analysis of the structure and properties of VDM® alloy C-4 after various treatments and methods of scanning and transmission electron microscopy has been shown that the main phase formed at 700 - 1000 ℃ is the σ-phase. However, this conclusion requires confirmation due to the locality of the methods used. An integral technique that allows one to identify the second phase formed in aging alloys is the X-ray phase analysis of the anode deposit.

Thus, the purpose of this work was the electrochemical extraction of the second phase from the VDM® alloy C-4 in the form of an anode deposit and its further study by scanning electron microscopy and X-ray phase analysis.

2. Material and methods

VDM® alloy C-4 after annealing served as the material of investigation in this work. The chemical composition of the alloy is shown in Table 1. The heat treatment scheme is shown in Figure 1.

Table 1. Chemical composition of VDM® alloy C-4[a], wt. %

C	Mn	Cr	Mo	Fe	P	Ti	Co	Si	S
≤0.009	≤1.0	14.5…17.5	14.0…17.0	≤3.0	≤0.020	≤0.7	≤2.0	≤0.05	0.010

[a]Note - base - Ni; alloy composition, wt. %.

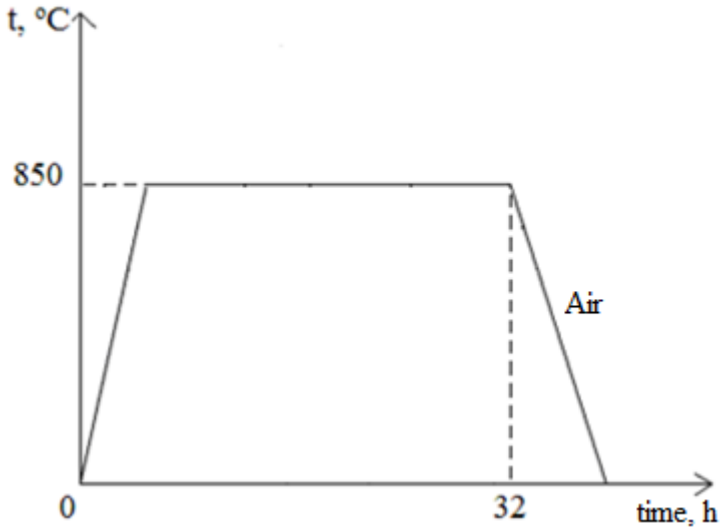

Figure 1. The heat treatment scheme

Figure 2 shows the scheme of an electrolytic cell which was used to precipitate the anode deposit.

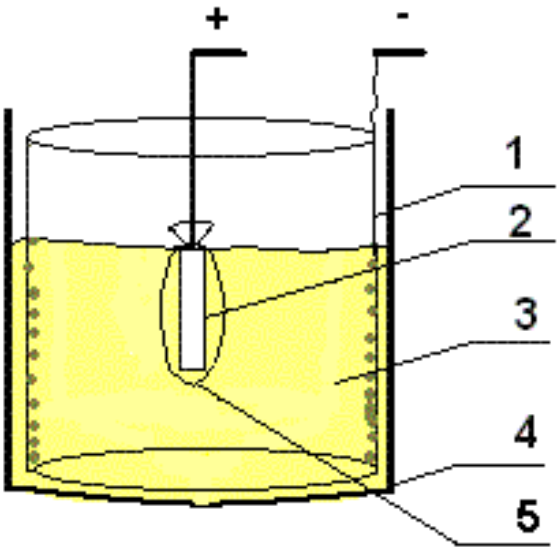

Figure 2 The scheme of an electrolytic cell: 1 - cathode; 2 - anode (sample); 3 - electrolyte; 4 - glass tumbler; 5 - collodion bag

A titanium sheet was used as a cathode (1). Anode (2), which is the studied VDM® alloy C-4, suspended on a copper wire, was placed in a collodium bag (5). The collodion bag was immersed in an electrolyte of 50% HCl + 50% H_2O (3) in a glass (4) with a diameter of 55 - 75 mm.

The precipitation of the investigated phase is associated with its low content in the alloy. Before electrolytic dissolution, the surface of the sample was preliminarily cleaned on an abrasive wheel. After the precipitation, the contents of the collodion bag were carefully poured into a clean vessel, in which it

was washed with distilled water. After the powder settled at the bottom, the water was poured off, and the contents of the glass were dried.

The studies were carried out on a Jeol JSM-6490LV scanning electron microscope equipped with an Oxford Inca Energy 350 energy dispersive microanalyzer.

X-ray phase analysis was carried out using a Bruker D8 Advance diffractometer in Kα Cu radiation in the range of 2θ reflection angles from 20 to 120 ° at voltage U = 40 kV, tube current I = 40 mA using Soller slits of the incident beam; the measuring diameter was 500 mm, with a step of 0.025 °.

3. Results and discussion

In the initial state, the structure of VDM® alloy C-4 is a solid solution based on nickel (figure 3). annealing at 850 ℃ for 32 hours led to the precipitation of the second phase along the grain boundaries (figure 4).

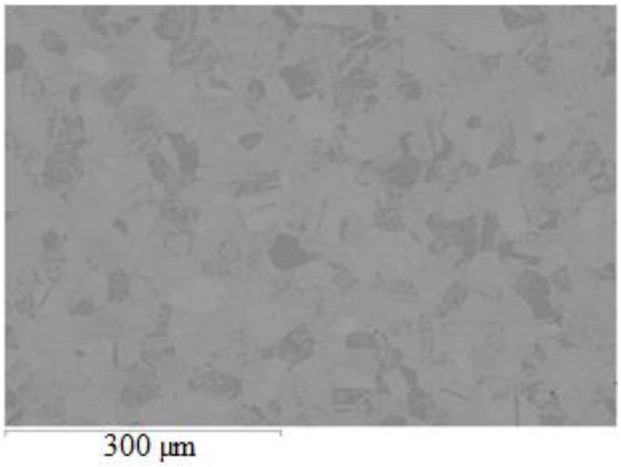

Figure 3. Structure of alloy VDM® ALLOY C-4 in the initial state

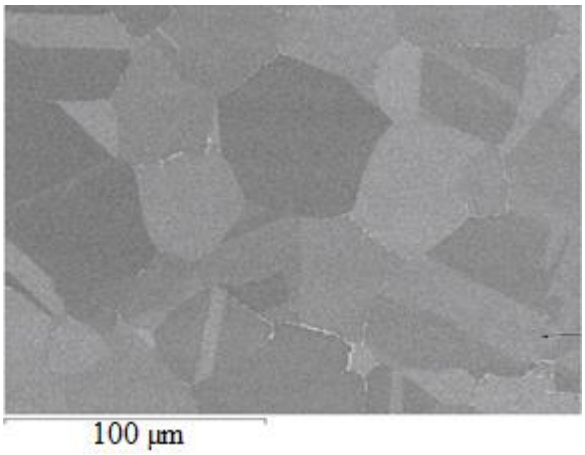

Figure 4. precipitation of the secondary phase in the structure of alloy VDM® ALLOY C-4 samples after annealing

Precipitation of the anode deposit was carried out after annealing. As a result, a powder composed of second phase particles was obtained. An electron microscopic image of the anode deposit is shown in figure 5. The shape of the particles is predominantly lamellar.

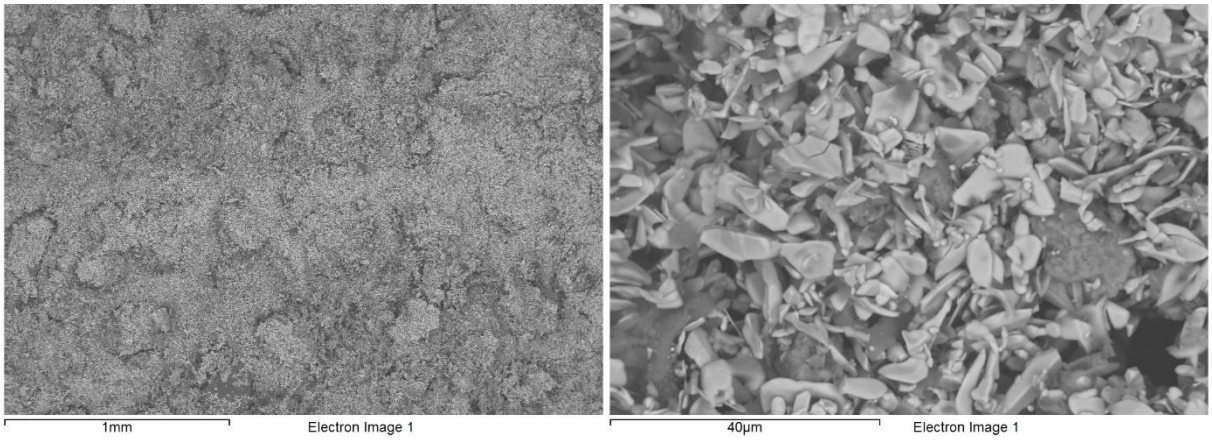

Figure 5. SEM images showing the precipitated deposit

X-ray spectral analysis of separate particles showed that they contain 33 …40 wt. % Ni, 31 … 42 wt. % Mo and 25…29 wt. % Cr. On the basis of these data, the points corresponding to the composition of the precipitated phase are plotted on the phase diagram (figure 6). Almost all points lie in the two-phase γ + P or three-phase region γ + P + σ. This suggests that the deposit consists of a mixture of P + σ phases.

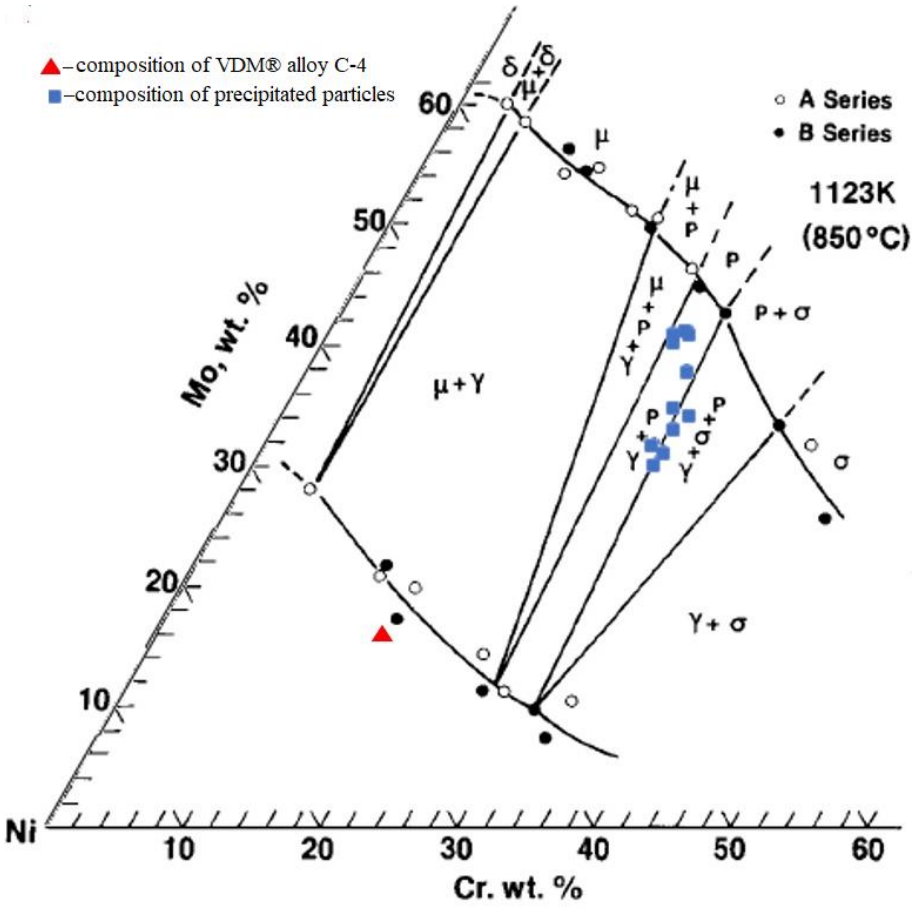

Figure 6. Ni-Cr-Mo phase diagram [6] with composition of VDM® alloy C-4 and composition of precipitated particles of this research

Figure 7 shows the XRD pattern of deposit. The experimental XRD pattern was compared with the known X-ray analysis (XRFA) data of the rhombic P-phase [9] and tetragonal σ-phase [10].

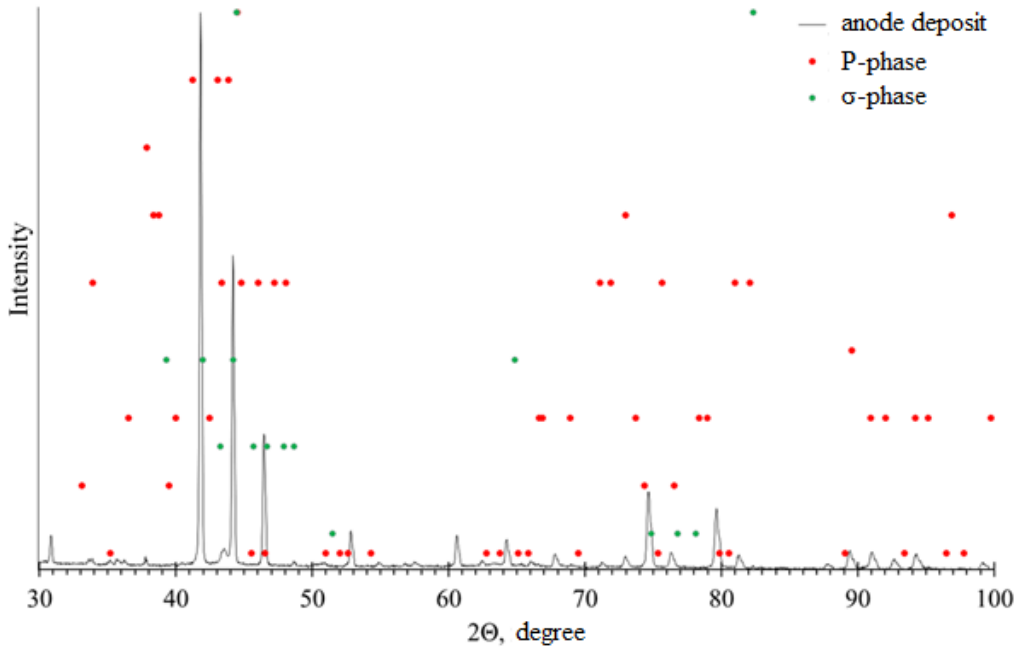

Figure 7. The XRD pattern of anode deposit

The values of the interplanar distances determined for the peaks in the XRD pattern are shown in Table 2. The most intense lines refer to the σ-phase. A less symmetrical P-phase lattice produces more reflections.

Table 2. Interplanar distances of the crystal lattice of anode deposit

d/n, Å	(hkl) Phase
2,898	
2,161	(410) σ
2,076	
2,050	(202) σ
1,955	(002) P, (411) σ
1,730	(380) P
1,527	
1,449	
1,379	
1,297	
1,271	(532) σ, (602) P
1,248	(711) P, (413) σ
1,204	(4 12 0) P
1,183	(004) P
1,096	(840) P
1,081	(831) P
1,065	
1,051	(6 11 1) P
1,012	

Thus, in VDM® alloy C-4, after annealing at 850 ℃ for 32 hours, the precipitation of the P-phase and σ-phase was observed.

4. Conclusions

- It was found by scanning electron microscopy that in VDM® alloy C-4 after annealing at 850 ℃ for 32 hours, intermetallic phases enriched with chromium and molybdenum are precipitated.
- The deposit precipitated from the alloy contains 33 - 40 mass. % Ni, 31 - 42 wt. % Mo and 25 - 29 wt. % Cr.
- Using X-ray analysis it was determined that the deposit consists of the P-phase and the σ-phase.

Acknowledgments

The work was carried out within the framework of the state assignment of the Russian Federation No. 0836-2020-0020 with the support of the project "Creation and operation of a network of international scientific and methodological centers for the dissemination of the best international practices for training, retraining and internship of advanced digital economy personnel in the fields of mathematics, informatics, technology" (Agreement No. 075-15-2019-1907 dated 09.12.2019)

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